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APPLICANT: ADVANCED NANO TECHNOLOGIES PTY LTD

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PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

"PROCESS FOR THE PRODUCTION OF ULTRAFINE PLATE-LIKE ALUMINA PARTICLES"

The invention is described in the following statement:-

PROCESS FOR THE PRODUCTION OF ULTRAFINE PLATE-LIKE ALUMINA PARTICLES

Field of the invention

The invention relates to a process for the production of substantially discrete ultra-fine plate-like particles of alumina with a high aspect ratio.

Background to the Invention

Plate-like morphology is realised as a result of preferential growth of particles in crystallographic directions parallel to certain planes and slower growth mechanisms in directions other than this plane.

It is well known that particles with a particular morphology can be generated by heat treatment in certain flux or diluent systems where the product phase is soluble in the flux or diluent. For example it has previously been shown that plate-like particles of bismuth tungstate can be grown during heat treatment of bismuth oxide and tungsten oxide in molten salt mixtures at temperatures above 650°C. Molten chlorides promoted plate-like growth, whereas molten sulphate salts did not. It is not known in the art to generate plate-like particles in solid state systems.

Plate-like particles have a significant potential for a wide range of applications including soft focus filler materials for cosmetics, polishing and lapping slurries, advanced ceramic materials, composites, hard coatings, paper coatings and substrate materials for pearlescent pigments.

Plate-like particles with a high aspect ratio and a low degree of agglomeration are particularly attractive for these applications. "Agglomeration" is a term that refers to the degree to which particles are clumped together or interlocked which increases the effective particle size. The degree of agglomeration of particles is routinely assessed using a combination of scanning electron microscopy and laser light scattering particle size analysis. Close agreement between the average particle size determined by these two methods indicates that the particles being tested are substantially discrete ie have a low level or degree of agglomeration.

Processes for the production of plate-like particles of alumina are known in the art. For example, platy alumina is commercially produced by the controlled calcination of aluminium trihydrate. A hydrothermal technique for the production of plate-shaped alumina particles is described in US 5,587,010. With known techniques, the particles tend to be agglomerated, requiring the use of expensive post milling and classification processes (see for example US 3,121,623 and US 5,277,702). The particles also tend to be of irregular shape and size, with minimum dimensions exceeding 1 micron and thus a relatively low aspect ratio.

Certain of the techniques directed specifically to achieving high aspect ratios and forming substantially discrete plate-like particles known in the prior art require uneconomical conditions of temperature and pressure to form plate-like particles. An example of such a technique is disclosed in US 5,702,519 (*Merck*) which describes a process for the production of non-aggregated plates of alpha alumina with high aspect ratios. The *Merck* patent discloses a process which involves the step of preparing aqueous solutions of water-soluble aluminium and titanium salts in which it is stated that it is important to ensure complete dissolution in solutions of these salts to avoid agglomeration of the product. The starting materials ie the salts are completely dissolved as a first step of the process and processing is preferably conducted at high temperatures between 900 and 1400°C and high pressures.

The present invention was developed with a view to providing a more cost-effective and controllable process for the production of substantially discrete plate-like particles with a high aspect ratio without restriction with regard to conducting the process in a liquid state.

Throughout this specification the term "comprising" is used inclusively, in the sense that there may be other features and/or steps included in the invention not expressly defined or comprehended in the features or steps subsequently defined or described. What such other features and/or steps may include will be apparent from the specification read as a whole.

Summary of the Invention

According to a first aspect of the present invention there is provided a process for the

production of substantially discrete plate-like alumina particles with high aspect ratio, the process comprising the steps of:

forming a mixture of substantially discrete nano-sized particles of an aluminium precursor compound having preferred crystallographic rapid and slow directions of growth, and a sufficient volume fraction of a diluent; and

heat-treating the mixture to form substantially discrete plate-like alpha alumina particles dispersed in the diluent.

Preferably, the process further includes the step of removing the diluent such that the substantially discrete plate-like alpha alumina particles are left behind.

The term "diluent" here is used to describe a substance in solid or liquid form that "dilutes" the mixture and is added to help maintain separation of the substantially discrete particles throughout the process. The diluent may react with the precursor aluminium compound or merely be present as a spectator. Preferably, the diluent is soluble in a solvent which selectively removes the diluent and does not react with alumina. More preferably the diluent is soluble in water or alcohol.

Preferably, the sufficient volume fraction of the diluent is at least 80%.

While a wide range of diluents may be used, the preferred diluents are selected to encourage plate-like growth of the alumina particles during heat treatment. The preferred diluent is a metal salt such as sodium sulphate, potassium sulphate or sodium chloride, with sodium chloride highly preferred as being cheap and readily available. A mineraliser in the form of a metal fluoride may also be added to the diluent to form a diluent-mineraliser system. The preferred metal fluorides are sodium fluoride, calcium fluoride, aluminium fluoride and sodium aluminium fluoride (cryolite).

The conditions for heat treatment of the dispersion are dependent on the choice of the diluent or diluent-mineraliser system. The advantage of using a diluent-mineraliser system is that the heat treatment may be conducted at a lower temperature than for a single diluent.

It is preferable that heat treatment be conducted below the melting point of the diluent(s)

or diluent-mineraliser system, or below the liquidus where d[illegible] mixture is a solid solution, such that sufficient solid diluent is present to keep particles separate during growth. It is equally possible for the step of heat treating the mixture to be conducted above the liquidus of the diluent(s) or diluent-mineraliser system. In the latter case, the process further includes the step of stirring the dispersion during heat treatment to minimise interlocking of the growing plate-like particles.

Any suitable process for stirring of the mixture may be employed including but not limited to mechanical mixing, rotation of the container, the use of convection currents, induction heating or any other method that imparts relative motion of the particles in the fluid.

The heat treatment temperature may be selected to control the relative amounts of gamma alumina particles and plate-like alpha alumina particles. Thus, for example, if a preferred product requires that only 50% of the particles be in the form of plate-like alpha alumina, the heat treatment would be conducted at a lower temperature than for a product requiring 90% plate-like alpha alumina particles. Thus the conditions for heat treatment of the mixture are dependent on the choice of the diluent or diluent-mineraliser system as well as the desired product phase(s).

The preferred aluminium precursor compound is aluminium hydroxide as aluminium hydroxide is cheap, readily available, easy to handle and readily dehydrates to form aluminium oxide.

Other suitable precursor compounds include aluminium sulphate, aluminium nitrate and aluminium chloride. With these precursor compounds, the process further includes the steps of milling the aluminium precursor compound and a suitable diluent such as sodium hydroxide in accordance with the method described in the applicant's International application WO 99/59754, the contents of which are incorporated herein by reference. Thus according to a second aspect of the present invention there is provided a process for the production of substantially discrete ultrafine plate-like alumina particles having a high aspect ratio, the process comprising:

milling a mixture of an aluminium precursor compound and a sufficient volume fraction of a diluent to form a dispersion of nano-sized particles of an intermediate

aluminium compound having preferred crystallographic rapid and slow directions of growth in the diluent; and

heat-treating the dispersion to convert the nano-sized particles of the intermediate aluminium compound to ultra-fine plate-like particles of alumina.

The step of heat-treating may be conducted simultaneously or subsequent to the step of milling.

Preferably the process further includes the step of removing the diluent such that ultra-fine plate-like particles are left behind in the form of an ultrafine powder. Preferably the step of removing the diluent includes the step of washing with a solvent which selectively removes the diluent phase while not reacting with the plate-like alumina particles.

The intermediate aluminium compound would typically be aluminium hydroxide or aluminium oxide.

Alternatively, the process described in WO 99/59754 may be used to produce the substantially discrete nano-sized particles of the alumina precursor compound as the starting material for the process according to the first aspect of the present invention.

According to a third aspect of the present invention there is provided a product in accordance with the process described above. Such a product is suitable for use in the following applications: soft focus cosmetics, pearlescent pigments, ceramic components and hard coatings.

Preferably the plate-like alumina particles have an aspect ratio of width to diameter of between 1:10 and 1:100 and more preferably between 1:20 and 1:50. The preferred aspect ratio depends on the particular application for which the powders are required. Preferably the diameter of the plate-like alumina particles is between 0.1 to 30 microns. Preferably the plate-like alumina particles have a thickness of between 50 and 200 nm.

Brief Description of the Drawings

In order to facilitate a more detailed understanding of the nature of the invention, preferred embodiments of the process for the production of ultrafine plate-like alumina particles will now be described in detail, by way of example, only, with reference to the accompanying drawings, in which:

Figure 1 is a Scanning Electron Micrograph of alumina plate-like particles in accordance with Example 1;

Figure 2 is a Scanning Electron Micrograph of alumina plate-like particles, many of which are interlocked due to intergrowth made in accordance with Example 2;

Figure 3 is a Scanning Electron Micrograph of alumina plate-like particles made in accordance with Example 3;

Figure 4 is a Scanning Electron Micrograph of alumina plate-like particles made in accordance with Example 4;

Figure 5 is a graphical representation showing the size distribution of the diameter of the plate-like particles of Figure 4;

Figure 6 is a Scanning Electron Micrograph of alumina plate-like particles made in accordance with Example 5;

Figure 7 is a graphical representation showing the size distribution of plate-like particles of Figure 6; and,

Figure 8 is a Scanning Electron Micrograph showing alumina particles made in accordance with Counter-example 1 with tabular morphology, low aspect ratio and interlocked clusters.

Detailed Description of Preferred Embodiments

This invention is derived from the discovery that in the process of heat treating a mixture of nanometre sized particles dispersed in a suitable diluent phase it has been observed that plate-like growth can occur for certain combinations of starting materials and diluents on increasing the heat treating temperature.

The choice of diluent has been found to govern the temperature at which the transformation to plate-like growth occurs during heat treatment. Suitable diluents include salts and mineralisers such as $NaCl$, Na_2SO_4, K_2SO_4, AlF_3, Na_3AlF_6 and mixtures thereof. Depending upon the choice of diluent, plate-like morphology can be generated either above or below the liquidus of the diluent. When heat treatment is performed

above the liquidus of the diluent, the plate-like alumina particles [illegible] to form interlocked clusters as a result of intergrowth in the liquid phase. To encourage separation of the plate-like particles, the heat treatment is performed in a stirred bath of liquid diluent. When heat treatment is performed below the liquidus of the diluent, intergrowth of platelets is avoided by virtue of the fact that sufficient solid diluent separates neighbouring platelets from one another during growth.

In one preferred embodiment of the present invention the starting material aluminium hydroxide is in the form of nano-sized particles dispersed in sodium chloride. The mixture is heat treated causing dehydroxylaton of the aluminium hydroxide. Nano-scale grains of gamma alumina form within the diluent material and subsequently form alpha-alumina platelets (α-Al_2O_3) as the temperature of the heat treatment is increased.

Throughout the following illustrative examples, aluminium hydroxide has been chosen as the aluminium precursor compound by way of example only and is not intended to limit the scope of the present invention in any way. These examples are intended merely to show the best method of producing plate-like alumina particles known to the applicant at the date of filing of the present application.

In each of the examples described below, the water-soluble diluent phase was removed from the alumina particles after heat treatment by washing six times with de-ionised water. Between subsequent washes the platelets were separated from the wash solution either by settling in a 30-litre drum or by centrifugation in a 40cc centrifuge tube, depending on the size of the sample. It is expected that a suitably qualified person may devise other methods for removing the diluent from the alumina particles without departing from the inventive concept of the present invention. For example, other solvents may be used. All such variations are considered to be within the scope of the present invention for which the following examples are for illustrative purposes only.

<u>Example 1:</u> $Al(OH)_3$ in Na_2SO_4 diluent, stirred during heat treatment

180g aluminium hydroxide and 820g sodium sulphate were milled for 1 hour at 400 rpm in a 7 litre attrition mill using 25 kg of 6.35 diameter stainless steel balls to form nano-sized particles of aluminium hydroxide.

900g of the resulting powder was added to a 4 litre alumina crucible containing 2.27 kg of pre-molten sodium sulphate at 1100°C. The mixture was mechanically stirred at 60 rpm by two alumina stirring rods during addition of the milled powder and for a further hour whilst the mixture was held at 1100°C.

X-ray diffraction and electron microscopy studies confirmed that the resulting material consisted of platelets of alpha alumina 0.5-3 microns in diameter with thickness 50-100 nm. The particles were essentially individual platelets. Figure 1 shows a typical scanning electron micrograph of this material.

<u>Example 2:</u> Al(OH)$_3$ in NaCl diluent without stirring

100g aluminium hydroxide and 1000g sodium chloride were milled for 2 hours at 600 rpm in a 7 litre attrition mill using 25 kg of 6.35 mm diameter stainless steel balls. The as-milled structure consisted of nano particles of aluminium hydroxide, approximately 5 nm in size embedded in the sodium chloride matrix.

The resulting powder was heat treated in a sealed container at temperatures between 600 and 1300°C. The samples calcined between 600 and 800°C consisted of separated equiaxed nano particles of gamma alumina. Calcining between 900 and 1200°C resulted in a mixture of gamma and alpha alumina. Calcination at 1300°C resulted in a single phase product which consisted of alpha alumina plate shaped particles 50-100 nm thick and 0.5-5 microns in diameter. Figure 2 shows a scanning electron micrograph of this material, many of the plates were found to be interlocked as a consequence of intergrowth.

<u>Example 3:</u> Al(OH)$_3$ in NaCl diluent, with mineraliser, solid state heat treatment leading to 0.5-5 micron platelets

1.04g aluminium hydroxide was milled with 6.88g NaCl and 0.08g cryolite (Na_3AlF_6) for 3 hours in a Spex mixer mill using 80g of 12.7 mm diameter stainless steel balls to form nano-sized particles of aluminium hydroxide. Cryolite is known to be soluble in sodium chloride, forming a eutectic system, with eutectic temperature 730°C.

A sample of the resulting powder was heat treated at 500°C for 30 minutes and washed in de-ionised water, in order to examine the particle size prior to transformation to alpha

phase. X-ray diffraction measurements confirmed that the resulting material was gamma alumina. Electron microscopy studies revealed that the particles were separated equiaxed nano particles approximately 5 nm in size.

The remaining powder was heat treated for 2 hours below the eutectic temperature, at 720°C. X-ray diffraction and electron microscopy studies confirmed that the resulting material consisted of platelets of alpha alumina 0.5-5 microns in diameter with thickness 50-100 nm. The particles were essentially individual platelets with low levels of aggregation. Figure 3 shows a scanning electron micrograph of this material.

Example 4: $Al(OH)_3$ in NaCl diluent, with mineraliser, solid state heat treatment below liquidus temperature leading to 0.1-9 micron plates

500 g aluminium hydroxide was milled with 4450 g sodium chloride and 50 g cryolite (Na_3AlF_6) for 90 minutes in a 33 litre attrition mill at 270 rpm, using 100 kg of 6.35 mm diameter stainless steel balls to form nano-sized particles of aluminium hydroxide.

The resulting powder was heat treated for 2 hours at 780°C. X-ray diffraction and electron microscopy studies confirmed that the resulting material consisted of platelets of alpha alumina 0.1-9 microns in diameter with thickness 50-150 nm. The particles were essentially individual platelets with low levels of aggregation. Figure 4 shows a typical scanning electron micrograph of this material. Fig 5 shows the platelet size distribution in the sample, determined by laser light scattering.

Example 5: Partially dehydrated $Al(OH)_3$ in NaCl diluent with mineraliser, heat treatment below liquidus temperature leading to 1-30 micron platelets

650 g aluminium hydroxide which had been dried to 23% mass loss at 230°C was milled with 4300 g sodium chloride and 50 g cryolite for 90 minutes at 270 rpm in a 33 litre attrition mill using 100 kg of 6.35 mm diameter stainless steel balls to form nano-sized particles of aluminium hydroxide. X-ray diffraction measurements showed that the starting hydroxide material was predominantly boehmite (AlOOH), with a small fraction of gibbsite ($Al(OH)_3$) remaining.

The resulting powder was heat treated for 2 hours at 780°C. X-ray diffraction and electron microscopy studies confirmed that the resulting material consisted of platelets of

alpha alumi[illegible]0 microns in diameter with thickness 50-200 [illegible] The particles were essentially individual platelets with low levels of aggregation. Fig 6 shows a typical scanning electron micrograph of this material. Fig 7 shows the platelet size distribution in the sample, determined by laser light scattering.

<u>Counter Example 1:</u> Use of insufficient diluent at milling leading to 'tabular' alumina

520 g aluminium hydroxide was milled with 460 g sodium chloride and 10 g cryolite for 1 hour at 500 rpm in a 7 litre attrition mill using 25 kg of 6.35 mm diameter stainless steel balls to form nano-sized particles of aluminium hydroxide. This mass ratio lead to a volume fraction of sodium chloride/cryolite diluent of approximately 50%.

The resulting powder was heat treated for 2 hours at 780°C. X-ray diffraction and electron microscopy studies confirmed that the resulting material consisted of alpha alumina. The resulting material had tabular morphology with a low aspect ratio and interlocked clusters. The plates were 1-5 microns in diameter and 0.25-1 micron thick. Fig 8 shows a typical scanning electron micrograph of this material.

<u>Counter Example 2:</u> Removal of diluent prior to heat treatment, plate-like morphology absent from product

1.04 g aluminium hydroxide was milled with 6.96 g sodium chloride for 3 hours in a Spex mixer mill using 80 g of 12.7 mm diameter stainless steel balls.

2 g of the milled powder was washed a single time using 12 ml de-ionised water, with the intention of removing 75% of the sodium chloride diluent. The powder was dried and heat treated at 1300°C for 1 hour. Any remaining sodium chloride diluent was removed by washing six times with de-ionised water.

X-ray diffraction and electron microscopy studies revealed that the resulting material consisted of porous particles of alpha alumina 10-300 microns in size, plate like morphology was not observed.

From the above examples and without wishing to be bound by theory the following factors contribute to the formation of substantially discrete ultra fine plate-like particles

with a high aspect ratio:

a) The initial particle size must be of nanometre dimensions. The minimum particle size determines the minimum dimension of the plate-like particle ie its thickness and in the limit of no growth in the direction of slow growth the minimum dimension of the geometrical particles is equal to the initial particle size.

b) The diluent phase should be present in sufficient amount relative to the nano-sized particles so that volume fraction is high enough for the growing plate-like particles to remain separated during heat treatment. Typically the volume fraction of the diluent phase should exceed 80% to ensure substantially discrete plate-like particles of the product phase.

c) It is preferable that the nano-sized particles be single crystals with crystallographic rapid and slow directions of growth. The crystal structure of the alumina is important in determining the morphology of the resulting particles.

d) The diluent should be chosen to promote plate-like growth of the particles during heat treatment. Specific salts and mineralisers have been shown to exhibit this property which, without wishing to be bound by theory, appears to be due to the stabilisation of particular interfaces during growth.

e) The heat treatment may be carried out either below or above the liquidus of the diluent. When heat treatment is carried out above the liquidus of the diluent, it has been found that plates tend to form interlocked clusters which is believed to be as a result of intergrowth in the liquid phase. Substantially discrete plate-like particles are produced by performing heat treatment in a stirred bath of liquid diluent to prevent such intergrowth. Stirring may be achieved by mechanical mixing, rotation of the container, the use of convection currents, induction heating or any other method that imparts relative motion of the particles in the fluid, to prevent interlocking of the particles.

f) When heat treatment is performed below the liquidus of the diluent, it is believed that intergrowth of plate-like particles is avoided by virtue of the fact that

suffici[illegible]lid diluent separates neighbouring plate-like[illegible]icles from one another during growth. Thus stirring is not required when the step of heat treatment is conducted below the liquidus of the diluent.

Numerous variations and modifications will suggest themselves to persons skilled in the relevant art, in addition to those already described, without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description.

Dated this 7th day of January 2003

<u>ADVANCED NANO TECHNOLOGIES PTY LTD</u>

By Its Patent Attorneys
GRIFFITH HACK
Fellows Institute of Patent and Trade Mark
Attorneys of Australia

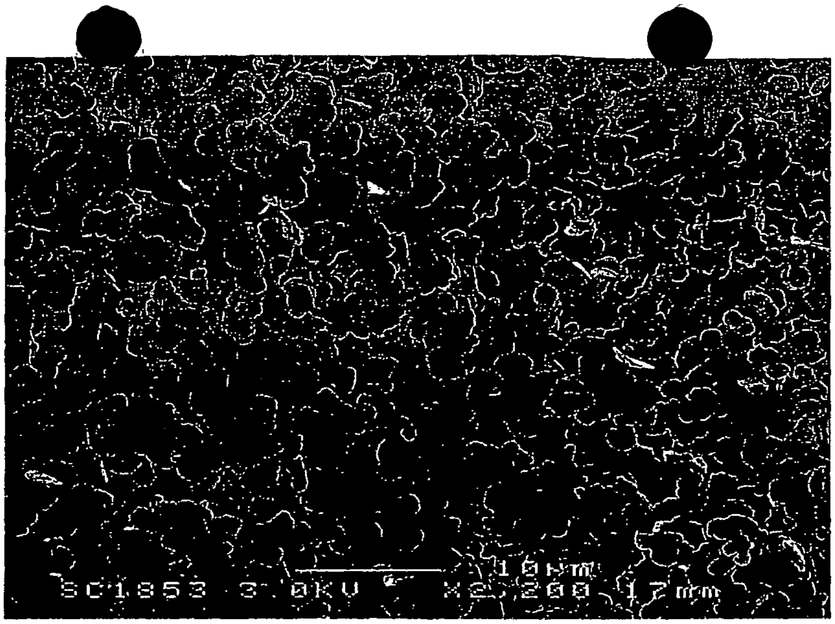

Figure 1

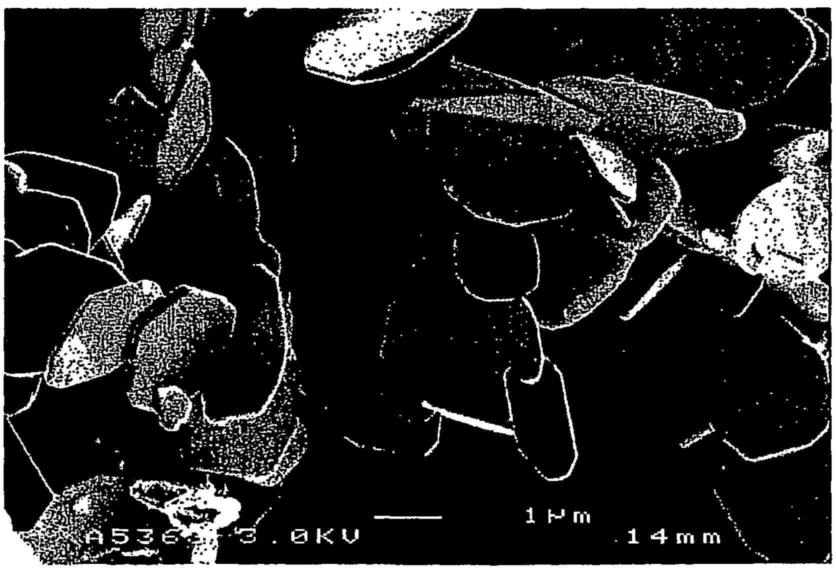

Figure 2

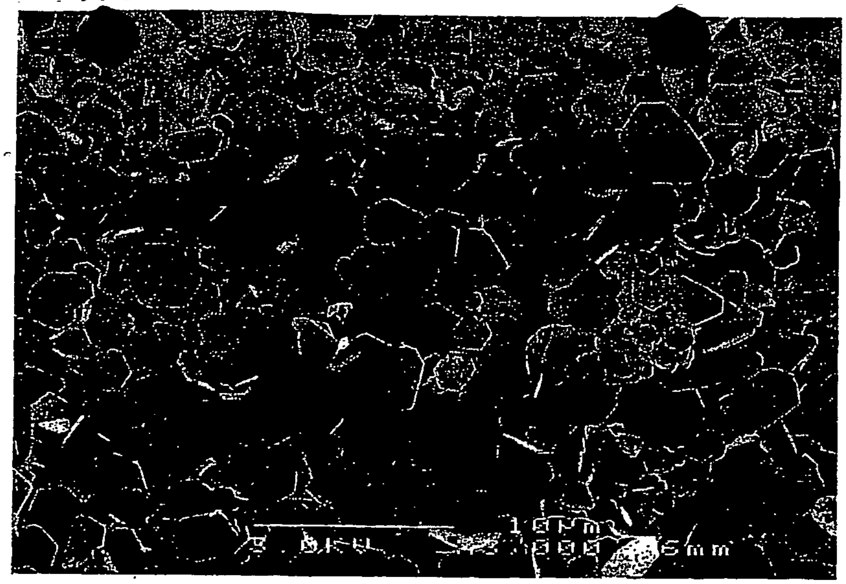

Figure 3

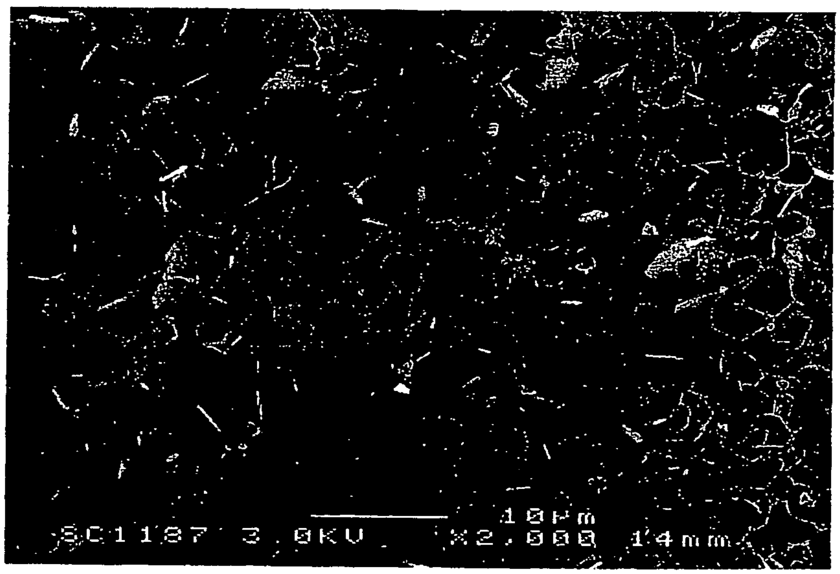

Figure 4

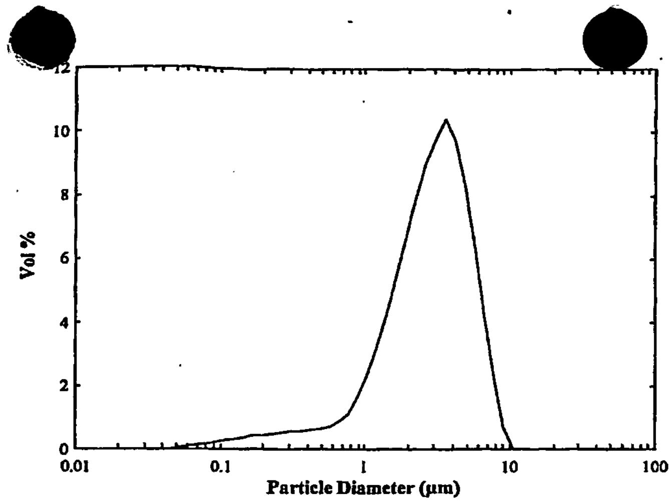

Figure 5

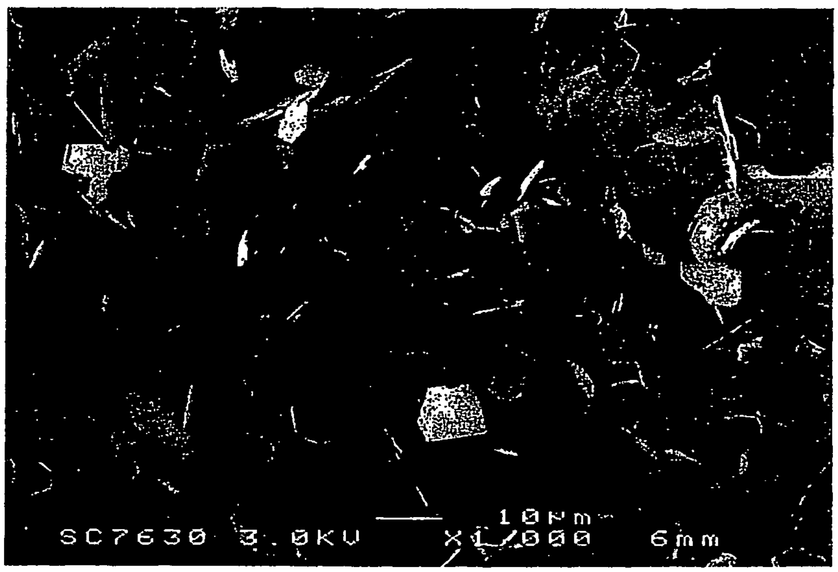

Figure 6

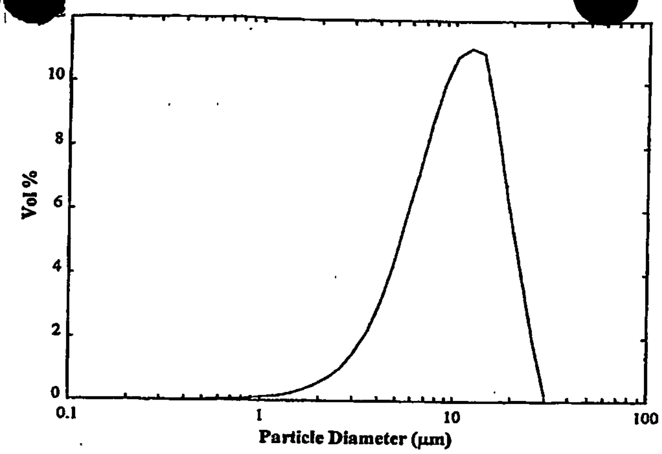

Figure 7

Figure 8